

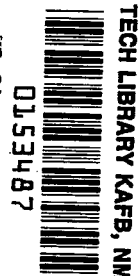
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VAPOR PRESSURE AND VAPOR FRACTIONATION OF TEKTITE MELTS

by L. S. Walter

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Washington, D. C.*



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SUMMARY

The total vapor pressure of philippinite tektite melts of approximately 70 percent silica has been determined for temperatures ranging from 1500 to 2100°C. It is 190 ± 40 mm Hg at 1500°C, 450 ± 50 mm at 1800°C, and 850 ± 70 mm at 2100°C.

The data were obtained by visually observing the temperature at which bubbles began to form for a constant low ambient pressure. By varying the ambient pressure a boiling point curve was constructed. This curve differs from the equilibrium vapor pressure curve because of surface tension effects. This difference was evaluated by determining the equilibrium bubble size in the melt and calculating the pressure due to surface tension. The latter was assumed to be 380 dynes/cm.

The relative volatility from tektite melts of the oxides of Na, K, Fe, Al, and Si has been determined as a function of temperature, total pressure, and, roughly, oxygen fugacity. The volatility of SiO_2 is decreased and that of Na_2O and K_2O is increased in an oxygen-poor environment. Preliminary results indicate that volatilization at 2100°C under atmospheric pressure causes little or no change in the percentage of Na_2O and K_2O . The Fe^3/Fe^2 ratio of the tektite is increased in ambient air at a pressure of 9×10^{-4} mm Hg ($10^{-6.5}$ atm O_2 , partial pressure) at 2000°C. This suggests that tektites either formed at lower oxygen pressures or were a product of the incomplete oxidization of a parent material with a still lower ferric-ferrous ratio.

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INTRODUCTION

In their aerodynamic analysis of tektites Adams and Huffaker (Reference 1) were forced to approximate the vapor pressure function for material of tektite composition. This approximation was based on the thermodynamic calculations of Schick (Reference 2), and possible errors resulted in a relatively great variability in the conclusions drawn from ablation analysis. It was hoped that pertinent experimental data could be obtained and applied.

The more accurate Langmuir and Knudsen techniques were discarded as being too costly in time and effort in view of the complex chemistry of tektites and the necessity, in these investigations, for data on the molecular weights of the species in the vapor and their accommodation coefficient. The "boiling point" method which was used and is described here was first thought to be too crude but worth using in the rather simple preliminary investigations. Because the results of the preliminary studies were interesting and encouraging, the study and the apparatus were enlarged.

If tektites have been thoroughly heated to high temperatures for moderate periods, it is conceivable that their bulk chemical composition has been modified by selective fractionation of vapor from the liquid phase. In this case, variations in the bulk composition of tektites cannot be compared with trends of igneous or sedimentary differentiation.

Vaporization differentiation trends are a function of temperature, total pressure, and oxygen pressure. Since earlier work on vaporization fractionation of tektite melts (References 3 and 4) was performed at atmospheric pressure under conditions of heterogeneous temperature distribution, a study under controlled conditions was undertaken.

The purpose of the fractionation study was to enable extrapolation from tektite composition to the parent composition. Although the results reported here are insufficient and too scattered to permit such an extrapolation, the study was rewarded by several unexpected results.

THEORY OF VAPOR PRESSURE DETERMINATION

Theoretically, a liquid boils at the temperature at which the vapor pressure equals the ambient pressure. Thus, by neglecting several factors it is possible to construct a vapor pressure curve by determining the boiling temperature as a function of ambient pressure. Three factors compromise this theoretical relationship:

1. The viscosity of the melt may prohibit the formation of bubbles, the melt "steaming" off the surface faster than bubbles can form. By using the function for viscosity determined by Chapman and Larson (Reference 5) which indicates a viscosity for tektite melts of approximately 500 poises at 1800°C, a pressure differential of 5 dynes/cm² is found to be sufficient to cause a bubble to expand 0.1 mm/sec. Since bubbles growing at rates less than this could be observed and were considered evidence of boiling, the effect of viscosity is considered negligible.
2. Another force exerted on the point at which a bubble forms during boiling is the weight of the overlying mass of melt. This factor might be an appreciable portion of the total pressure on this point when the ambient pressure is reduced to a few millimeters of mercury, or when the column of liquid above the point is quite high. Since the melts studied were no greater than 2 mm thick, the weight of the overlying material (under the assumption of a specific gravity of 2.5 gm/cm³) was no greater than an equivalent pressure of 0.4 mm Hg.
3. The final factor in the divergence of the boiling point from the vapor pressure determinations is the surface tension. This factor, σ , is related to the pressure it exerts on a point in the melt, P_s , by the relationship

$$P_s = \frac{2\sigma}{r},$$

in which r is the radius of a bubble in the melt. The pressure due to surface tension will cause bubbles with a radius less than a critical value to diminish in size, whereas those with greater radii will expand. For a value of 380 dynes/cm (on the basis of an experimental determination on a tektite by Chapman, personal communication, 1963) for the surface tension (variations of 50 dynes/cm in this figure yield results which are still well within the stated limits of error) and a value of 0.005 cm for the bubble radius, it was calculated that corrections for σ would be about 100 mm Hg—an appreciable error in the boiling point determinations. The error was obviated by the experimental determination of the critical bubble size and the calculation of P_s . Although surface tension varies as a function of temperature, this was neglected since it would involve a second order correction in the vapor pressure determination, unwarranted within the limits of error.

APPARATUS AND EXPERIMENTAL PROCEDURE

Preliminary studies were carried out in a vacuum coating unit consisting of a roughing pump, 4 inch oil diffusion pump, steel baseplate, and 18 inch diameter glass bell jar. Initial attempts to

heat the sample in tungsten crucibles by resistance heating of a small furnace of tungsten wire failed because conductive transfer of heat in a vacuum is quite low. Sample temperatures never exceeded 600°C although the windings were at 2600°C and only $1/8$ inch away. The final design of this apparatus utilized a single tungsten strip as a sample container and heating element, 3 inches long, 0.004 inch thick, and $1/2$ inch wide. This strip was necked down to $3/8$ inch for the central $3/4$ inch to produce a hot spot and eliminate excessive heating of the electrodes, which were made of steel. The sample was contained in a $1/8$ inch deep depression in the center of the strip, which was formed by pressing the strip in a mold at about 400°C . Discussion of this apparatus is limited here, since it was used only for the preliminary runs and one of the runs discussed in this paper.

All the other runs reported here were made in an apparatus, illustrated in Figure 1, which included an iridium crucible as the sample container. Although the use of iridium was limited to temperatures below 2350°C , it had the advantage of being less reactive than tungsten. Since the preliminary results indicated that the vapor pressures of tektites were greater than originally thought, it was possible to reach sufficiently high temperatures with iridium crucibles heated by a 10 kw induction heater.

Iridium crucibles were fabricated from a 0.001 inch thick sheet, by simply pressing a $1/4$ inch diameter ball bearing into the center of a $1/2$ inch diameter iridium disc (previously annealed at $\approx 1800^{\circ}\text{C}$) supported on a semihard rubber pad. Many of the crucibles were made from a 0.004 inch thick sheet and these had to be annealed, pressed with a 1 inch ball bearing; annealed, pressed with a $3/4$ inch ball bearing; etc. The size of the ball bearing was continually decreased until a shallow dish was formed. The end product was a dish a little over $1/4$ inch in diameter and about $1/8$ inch deep in the center. The iridium dishes were re-used, being cleaned in HF after each vapor pressure determination. Those used in the fractionation studies had to be destroyed during sample removal.

The crucibles were placed on zirconia powder contained in the flared end of a silica-glass tube. This tube and the crucible were then enclosed in a 1 inch diameter silica-glass tube about 12 inches long and sealed on one end by an optically smooth glass disc. The lower end of the 1 inch tube was then sealed with wax to the vacuum system, which consisted of a roughing pump and a 2 inch diameter air-cooled diffusion pump.

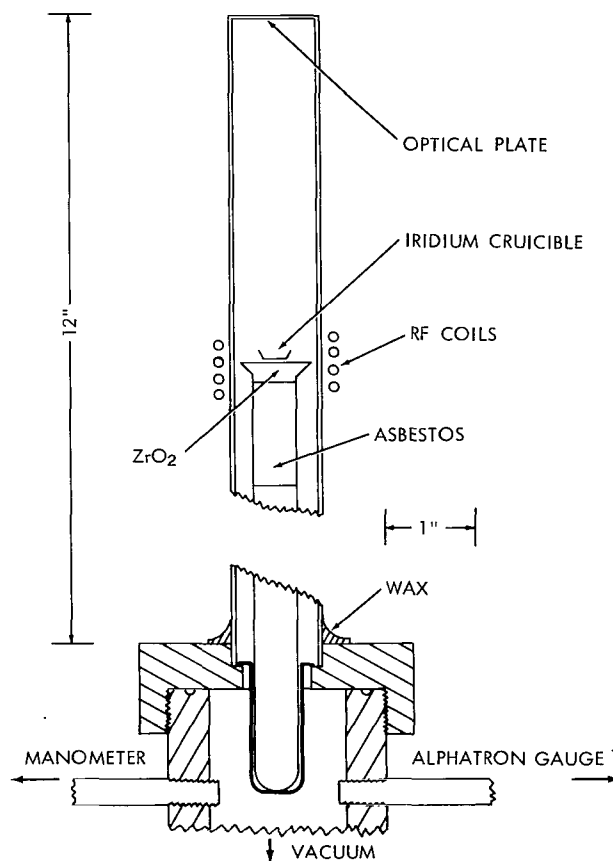


Figure 1—Diagram of the apparatus in which samples were heated in iridium crucibles by an induction furnace.

Continuous visual observation of the sample and temperature measurement were made with an optical pyrometer fitted with a close-up lens. The sample in the vertical tube was observed with the horizontal optical pyrometer through a 45 degree prism.

As indicated, it was necessary to measure the size of the bubbles produced in the boiling process. In this case a semitransparent 45 degree prism was substituted for the simple prism normally used and the image of a graduated reticle was superimposed on the image of the sample in the pyrometer. The brightness of the sample was so much greater than that obtainable for the reticle that an intermediate standard, the V-shaped filament of the pyrometer, was calibrated (in terms of its apparent size when superimposed on the sample image) by using the reticle as a primary standard. The diameters of the bubbles varied between 1 and 3 wire diameters, corresponding to about 0.003 cm.

PRESSURE AND TEMPERATURE CALIBRATION

Most of the pressure measurements were made with a mercury manometer considered accurate to within 2 mm Hg. Pressure measurements below 10 mm were made with an alphanatron ionization gauge considered accurate to within 10 percent.

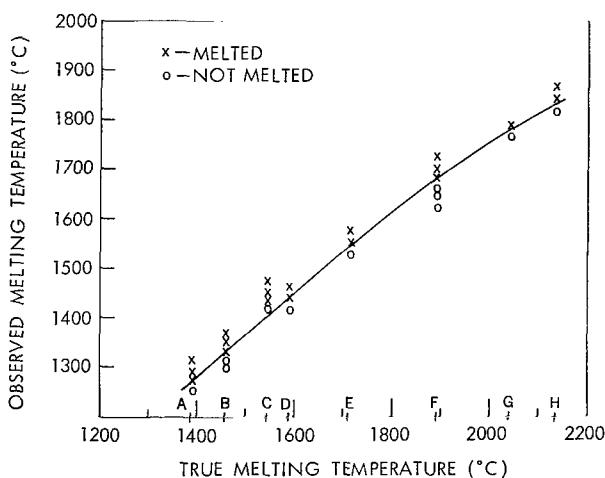


Figure 2—Temperature calibration curve showing true vs. apparent melting temperatures for the following oxides: A— $\text{CaMgSi}_2\text{O}_6$; B— CaMgSiO_4 ; C— CaSiO_3 ; D— $\text{Ca}_2\text{Al}_2\text{SiO}_7$; E— SiO_2 ; F— Mg_2SiO_4 ; G— Al_2O_3 ; H— MgAl_2O_4 . Circles indicate that the oxide did not melt and crosses indicate melting.

The entire temperature measurement system was calibrated at one time, based on the determination of the apparent melting temperatures of oxides with known melting points (Figure 2). Since the composition and therefore the emissivity of the sample material was a variable, it was decided to calibrate the temperature of the sample on the basis of the brightness temperature of the rim of the crucibles. Variations in the pyrometer, emissivity corrections for the particular shape of the iridium crucible, and absorption corrections for the prism and the viewing disc in the silica-glass tube were calibrated simultaneously, and this system was kept constant throughout the study.

There are several indications of the accuracy of this calibration. Little reaction occurred between the oxide and the iridium

crucible; because calibration was carried out at atmospheric pressure, there was probably little dissociation before melting and therefore no lowering of the true melting points. The smoothness of the calibration curve indicates that the calibration is at least internally consistent.

Temperature differences of about 30°C could be measured on an empty crucible at the temperatures at which the runs were made. Greater variations, however, can be expected in and through noncirculating material contained in the crucible, because of the low thermal inertia of the system. The significance of this is mitigated by two factors. The material investigated is boiling and convecting, and the material and thermal transfer tend to iron out the thermal gradient. More important is the fact that the sample will be hottest and will boil first where it is in contact with the crucible. Indeed, all calibrations were made under the same condition, namely the determination of the melting point at the hottest point in the sample; i.e., near the crucible. Thus variation due to the thermal gradient is compensated by the method of calibration. It is believed that the temperatures were accurate to within 25°C.

BOILING POINT AND VAPOR PRESSURE DETERMINATIONS

Since it was not possible to obtain a large amount of analyzed tektite material for the entire vaporization study, one rather large philippinite was used to obtain the vapor pressure curve. Both the refractive index (1.510 ± 0.005) and density (2.44 gm/cm^3) were determined for the specimen, and they agreed with each other according to curves presented by Chao (Reference 6). The values indicate a silica content of 70-72 percent by weight. Additional runs were made on two bediasites of extremely divergent compositions and on an obsidian sample which, after being crushed, was dried at about 500°C for several days. The purpose of these runs was to show the effect on the vapor pressure of variations in composition. The chemical analyses of these specimens are given in Table 1. The tektite material used in the investigation was prepared by dry grinding to a fine powder in an agate mortar.

In the determination of the boiling point, the powdered sample in the crucible, under vacuum, was gradually heated until it became fluid. Following this the temperature was slowly raised and recorded until boiling was observed. It was often possible to reverse the boiling process several times before fractional volatilization resulted in a significant increase in the boiling temperature. The critical bubble size and the pressure due to surface tension were determined in several steps: (1) the sample temperature was raised until bubbles formed in the melt; (2) the temperature was lowered and shrinking bubbles in the melt were sought; (3) the temperature was raised a

Table 1
Analyses of the Materials Used
In Vapor Pressure Determination
(Analyses by the U. S. Geological Survey).

Component	Composition (percent)		
	Bediasite B-105	Bediasite 30775-77	Grey Obsidian TM-2 (partial analyses)
SiO ₂	73.36	80.17	72
Al ₂ O ₃	16.04	11.19	13.8
Fe ₂ O ₃	0.31	0.18	{ 0.8
FeO	4.81	2.82	
CaO	0.61	0.56	0.6
MgO	0.75	0.37	0.1
MnO	0.03	0.04	0.08
BaO	0.06		
Na ₂ O	1.44	1.53	
K ₂ O	1.93	2.24	3.2
P ₂ O ₅	0.03	0.03	
TiO ₂	0.87	0.60	<0.2
H ₂ O ⁺	(51 ppm)		
H ₂ O ⁻	(51 ppm)		
	100.24	99.73	<90.78

small amount (about 30°C) to see whether the bubbles would contract and expand in phase with the small fall and rise of temperature. When these events were observed (they were observed in approximately 50 percent of the runs) the critical size (the size above which the bubbles seemed to grow and below which they seemed to contract) was determined with respect to the width of the pyrometer filament. The pressure due to surface tension was then computed and this value was added to the ambient pressure in order to obtain a closer value for the vapor pressure of the melt.

Data for the runs obtained by these methods appear in Tables 2 and 3. The results are illustrated in Figure 3. The lower curve in this figure is for the boiling point determination and does not take into account corrections for surface tension. At higher temperatures, it is relatively closer to the upper curve which takes into account surface tension and is based on the critical bubble size determinations. Brackets for the lower curve indicate not limits of error but the temperature limits of observation. That is, the higher temperature points on the brackets indicate those temperatures at which the samples first were observed to boil; the lower points indicate the highest temperatures at which the samples did not boil. The sharp drop in the lower boiling point curve is a result of the increased relative importance of the surface tension correction at lower pressures. Uncertainty of the vapor pressure values at the lowest temperatures is increased by the possibility that the temperatures are below the liquidus temperatures for these silicic compositions.

Table 2
Boiling Point Determinations

Pressure (mm Hg)	No Boiling (°C)	Boiling (°C)
2.8	1420	1445
4.	1320	1340
7.6	1440	1475
7.6	1455	1465
7.4	1465	1495
12.	1350	1370
10.	1455	1475
18.	1340	1355
160.	1460	1500
22.	1435	1480
25.	1455	1495
26.	1445	1500
32.	1425	1475
47.	1495	1510
52.	1455	1485
70.	1455	1485
98.	1475	1510
120.	1510	1520
140.	1600	1615
120.	1620	1630
198.	1590.	1620
190.	1665	1695
210.	1715	1735
400.	1805	1835
598.	2015	2135

The log of the vapor pressure is plotted against the reciprocal temperature in Figure 4. In Figure 5 the results of the runs on the bediasite and obsidian samples are superimposed on the curves for the philippinite sample. It appears that by this method it is impossible to distinguish any differences in the vapor pressures of these materials and, within the limits of error, the results fall on

Table 3
Vapor Pressure Determinations
Corrected for Surface Tension

Ambient Pressures (mm Hg)	Temperature (°C)	Radius (cm)	Vapor Pressure (mm Hg)
166	1485	0.008	238
80	1435	0.0075	156
110	1525	0.008	181
126	1560	0.007	208
145	1605	0.006	240
318	1575	0.015	356
300	1725	0.0075	376
380	1775	0.006	475
500	1890	0.005	610
312	1620	0.006	412
760	2170	0.009	828

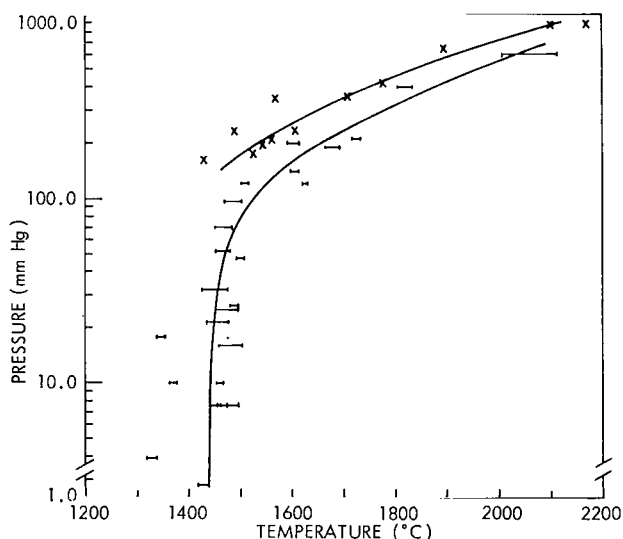


Figure 3—Boiling point (lower) and critical bubble size (upper) curves for philippinite with 70-72% silica. The upper curve is considered to be the vapor pressure curve for the material. The brackets, which determine the position of the lower curve, indicate the boundary limits of observations, i.e., above which the melt was observed to boil and below which it did not boil.

the philippinite curves. The limits of error, however, are quite large, and significant differences, especially in terms of fractional volatilization, may exist among these melts.

DISCUSSION OF THE VAPOR PRESSURE RESULTS

One important consideration in the interpretation of the results of the boiling point and equilibrium bubble size determinations is the possibility that the observed bubbles are caused by normally volatile constituents (H_2O , CO_2 , etc.) dissolved in or adsorbed onto the grains of the glass. Several observations, however, militate against this possibility:

1. Tektites boil in spite of their exceptionally low content of normally volatile constituents.
2. The boiling points of tektites are, in some cases, higher than obsidian, which probably has a far greater content of normally volatile constituents.
3. One run was made on a single sliver of philippinite (3/16 inch in diameter and about 1 16 inch thick). At a low pressure (1 mm Hg) this sample began to boil at a temperature between 1400 and 1500°C.

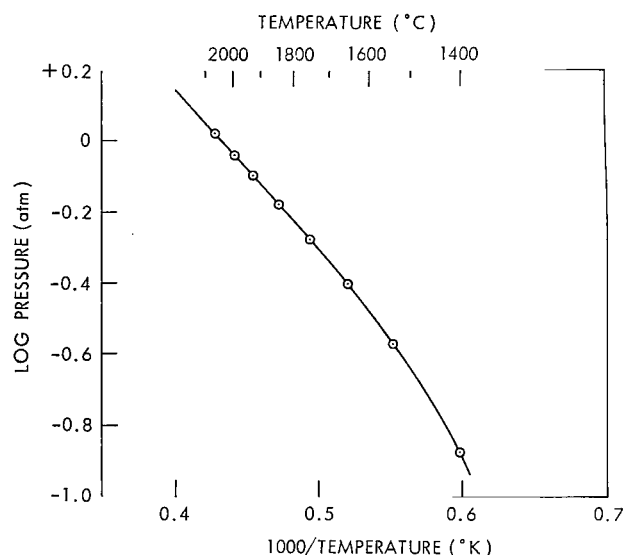


Figure 4—The vapor pressure curve of Figure 3 plotted for log pressure vs. the reciprocal temperature.

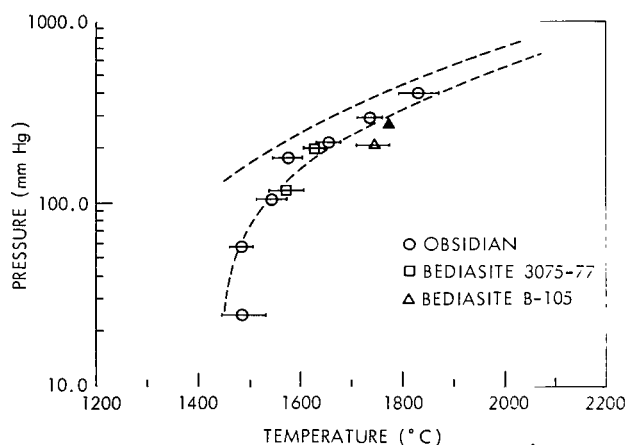


Figure 5—Results of the vapor pressure and boiling point determinations on two bediasites and an obsidian. For purposes of comparison, the curves of Figure 3 are reproduced as dashed lines. The determination shown for the bediasite without limits of error was made by using the boiling point method corrected for the surface tension effect.

4. The rapid expansion over a very short temperature interval (see Figure 2) cannot be ascribed to the PVT expansion of small bubbles in the melt because of rising temperature.
5. If, at constant pressure, the temperature is raised considerably above the boiling point, the melt will continue to boil until it is vaporized.
6. If, at constant pressure, the temperature is raised slightly above the boiling point, boiling will cease after a while. But it resumes if the temperature is raised again. The more volatile fraction of the melt is being distilled off.
7. Although a completely liquid melt forms at temperatures near 1500°C, initial boiling may take place at considerably higher temperatures.

An interpretation that the bubbles are caused by some dissociative reaction in the melt with a consequent release of a volatile phase is possible of course. The observed boiling point curve then would be interpreted as a PT dissociation curve but, thermodynamically, there is no distinction between this and a vapor pressure curve, the pressure necessary for reversing the dissociation being the vapor pressure of the substance.

VAPOR FRACTIONATION

In all, six runs were made in which the change in chemical composition of tektite melts due to fractional volatilization was studied. Five were made in iridium crucibles and were heated with an induction furnace. One was made in a tungsten crucible, which also served as the heating element, in a vacuum coating unit. The apparatus has been described in a preceding section. In a continuing study an attempt will be made to precipitate the vapor in a cold trap and study its structure and composition.

The accuracy stated for temperature and pressure determinations in the section on vapor pressure measurements also holds for the present investigation, even for the run in a tungsten container. The weight loss was determined by weighing the samples before and after heating. Determinations on empty crucibles indicate a maximum of 1 mg weight loss, which has little effect on the results. Small amounts of impurity in the zirconia substrate resulted, occasionally, in the clinging of small specks of zirconia to the iridium, but the total amount of such material was never greater than a milligram. Thus, this had only a minor effect on the apparent weight loss since the amount of sample was always more than 100 mg. The residual in the chemical analyses can be attributed only partially to CaO and MgO.

CHEMICAL COMPOSITION OF SAMPLES AND RESIDUA

Four tektite melts were made from portions of two previously analyzed philippinites, Pp-163 and Pp-216 (Reference 7). Each melt, weighing approximately 100 mg, was analyzed for alkalis, total iron as Fe_2O_3 , ferrous oxide, silica, and alumina. The paucity of sample sizes permitted only single determinations of most of these constituents. The envelopes of iridium and tungsten containing the melts were peeled back and the melts were transferred to a boron carbide mortar, ground, and sieved through 92 mesh bolting cloth in a plastic holder.

Approximately 10 mg of the ground samples were dissolved in perchloric and hydrofluoric acids. The amount of alkalis was determined by the flame photometer on an aliquot of the solutions. On another aliquot total iron as Fe_2O_3 was determined spectrophotometrically with ortho-phenanthroline.

The ferrous oxide content was determined in each of the samples on portions weighing from 8 to 10 mg by using a semi-microvolumetric method (Reference 8). These results were confirmed by another run of each sample with an improved technique of the same method (Reference 9).

The silica and alumina contents were determined spectrophotometrically on another 10 mg portion of each sample. The samples were fused with sodium hydroxide and dissolved in hydrochloric acid. The silica content was determined on an aliquot of the solution by the molybdenum blue method and the alumina content by the color produced with alizarin red S (Reference 10).

The accuracy of these determinations was monitored by simultaneously running samples of rock standards G-1 and W-1 (Reference 11), and a 1 + 1 composite sample of these.

DISCUSSION OF THE VAPOR FRACTIONATION EXPERIMENTS

Chemical analyses of the starting materials and the products of the runs are listed together with run conditions and other pertinent information in Table 4. The first four runs, $V_1 - V_4$, were designed to illustrate fractionation under varied but controlled conditions. The last two, V_5 and V_6 , were made to check the surprising results obtained for the relative volatilization of the alkalis.

Table 4
Chemical Analyses of Tektites Before and After Vaporization Fractionation
(Pp-216 for V_1 and V_2 ; Pp-163 for V_3 and V_4 ; Pp-0 for V_5 and V_6)

	Pp-216	V_1	V_2	Pp-163	V_3	V_4	Pp-0	V_5	V_6
Temperature ($^{\circ}\text{C}$)	-	2010-2080	2060-2090	-	2050	1780	-	2050	2050
Pressure (mm Hg)	-	1.5×10^{-3}	10^{-3}	-	760	9×10^{-4}	-	760	760
Crucible	-	W	Ir	-	Ir	Ir	-	Ir	Ir
Time (min)	-	8	5	-	8	30	-	4	20
Weight loss (percent)	-	15.2	22	-	9.2	2.5	-	6.6	27
SiO_2 (percent)	70.56	70.4	67.3	71.68	68.5	71.00	-	-	-
Al_2O_3 (percent)	13.6	14.1	16.9	12.41	11.9	12.4	-	-	-
K_2O (percent)	2.59	0.91	0.99	2.12	2.35	1.88	2.27	2.26	2.29
Na_2O (percent)	1.37	0.06	0.11	1.52	1.23	0.60	1.29	1.31	1.32
FeO (percent)	4.84	4.84	{2.99* 3.14	4.68	2.99	4.33	-	-	-
Fe_2O_3 (percent)	0.21	-	{0.59 0.42	0.30	2.08	0.73	-	-	-
Component Total (percent)	93.17	90.31	88.82	92.71	89.05	90.94	-	-	-
$\text{Fe}_2\text{O}_3/\text{FeO}$	0.0435	-	{0.198- 0.132	0.0641	0.70	0.168	-	-	-

*Braces indicate replicate analyses.

A discrepancy in the vapor fractionation method is implicit in the analyses summations of Table 4. These sums show a slightly greater decrease in the percentages of the constituents in the residual fraction than is consistent with the total weight loss. This discrepancy can be attributed to the sum of small errors in the analyses and to the inclusion of small amounts of crucible material with the material analyzed. One or two milligrams of crucible material retained after sample separation could account for the apparent excess loss through volatilization and would mean that the analyses of the constituents of the residuum are 1 or 2 percent lower than the true amount.

The results of fractionation experiments $V_1 - V_4$ are illustrated in Figures 6-9. If the loss of a constituent were a function only of the amount in the melt, the log of the constituent in the residuum would be a linear function of the total weight loss. The linear plots of Figures 6-9 assume that this relationship holds, at least to a first approximation. The loss of a constituent, however, is also a function of the other components of the melt, resulting in deviations of the curves from linearity. Figures 6-9 assume that a linear relationship holds, at least to a first approximation. The arrows indicate the total weight loss of each sample.

The results of additional runs to check alkali loss, V_5 and V_6 , are shown in Figure 8 as dashed lines. Since neither run showed any change in soda or potash content (although the total weight loss was 6.6 and 27 percent respectively), the results for the two runs are colinear. In all cases, the total iron is calculated and plotted as Fe_2O_{3t} .

The conditions of runs V_1, V_2 , and V_3 represent a progressive and substantial increase in oxygen fugacity. In the case of V_2 this factor must be extremely low since the tungsten crucible must soak up almost all oxygen as it becomes available. If the mole fraction of oxygen in the atmosphere in the case of V_2 is assumed to be the same as that in air, the partial pressure was approximately 2.8×10^{-7} atm. In the case of V_3 , the partial pressure of oxygen must have been 0.21 atm. Run V_4 is not highly significant since the low vaporization loss makes the analytical errors more important.

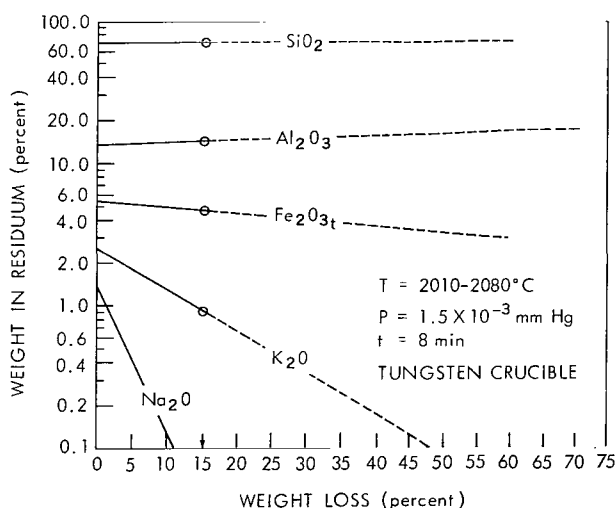


Figure 6—Results of vapor fractionation experiment V_1 .

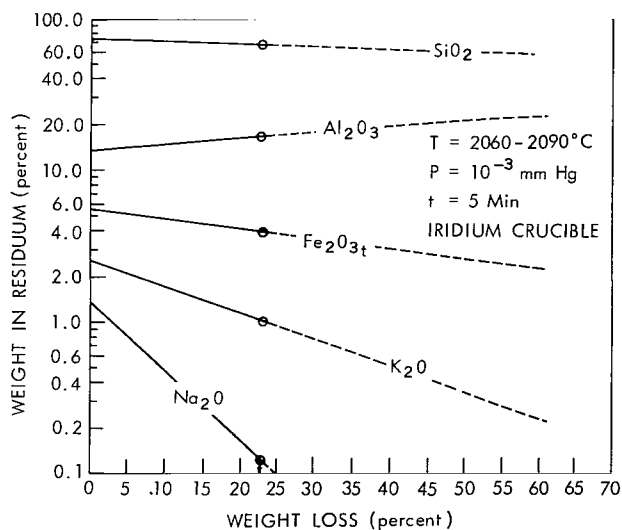


Figure 7—Results of vapor fractionation experiment V_2 .

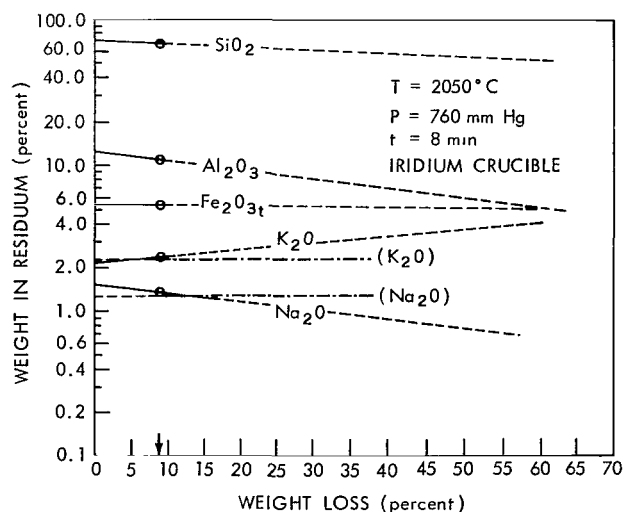


Figure 8—Results of vapor fractionation experiment V_3 .

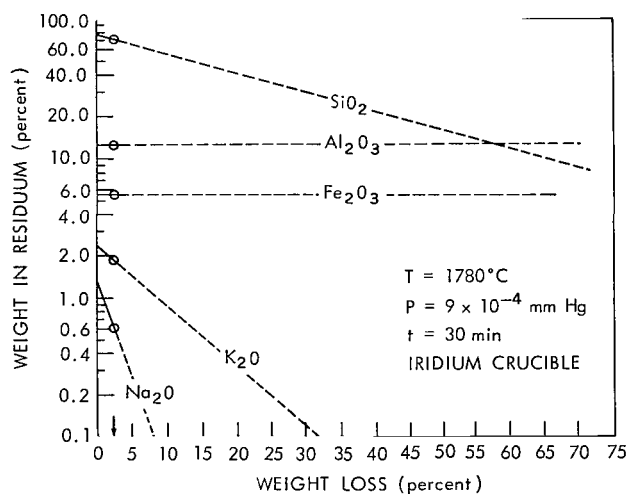


Figure 9—Results of vapor fractionation experiment V_4 .

Suggestions that the relative volatility of silica from tektite melts would be increased under conditions of extremely low oxygen pressure (increased loss of SiO) are contradicted by runs V_1 , V_2 , and V_3 . Indeed, the data show that the relative volatility of silica is increased at higher oxygen pressures. It is interesting to note that the percentage of silica decreases under all but the most reducing conditions.

The results on alkali volatilization are interesting and somewhat surprising. The relative volatilities of Na_2O and K_2O increase with decreasing oxygen fugacity and, in fact, there is no significant relative loss of alkalis in runs made at atmospheric pressure ($P_{\text{O}_2} = 0.21$ atm). Runs V_5 and V_6 were made to check this point and, as illustrated in Figure 8 no change in composition was detected. These data agree with recent analyses of australite flanges and cores which indicate no constant relationship between the alkali contents of flange-core pairs (F. Cuttitta, private communication). The lack of fractionation of the alkalis under these conditions suggests that the alkali percentage was reduced to the present value by fractional volatilization and has achieved an equilibrium distribution between melt and vapor at atmospheric pressure. This, of course, is only an approximate relationship since the vaporization experiments show that the bulk composition of the melt does change, even at atmospheric pressure. And this, at least, necessitates a change in the mole fraction of alkalis in the melt in order to maintain the observed constant weight fraction. On the other hand, it is probably significant that the constituents generally considered to be most volatile are, under certain conditions, not depleted in the melt.

The ratio of K_2O and Na_2O also shows a constant relationship with P_{O_2} , as shown in Figure 10. The value $\text{K}_2\text{O}/\text{Na}_2\text{O}$ decreases with increasing oxygen pressure.

The values for the ratio $\text{Fe}_2\text{O}_3/\text{FeO}$ shown in Table 4 indicate that in all cases (except the extreme reducing conditions of V_1) the ratio increased. Consideration of these data must place some limitations on the theories of tektite formation. If a terrestrial starting material is proposed, it is difficult to hypothesize a ferric-ferrous ratio lower than that found in tektites.

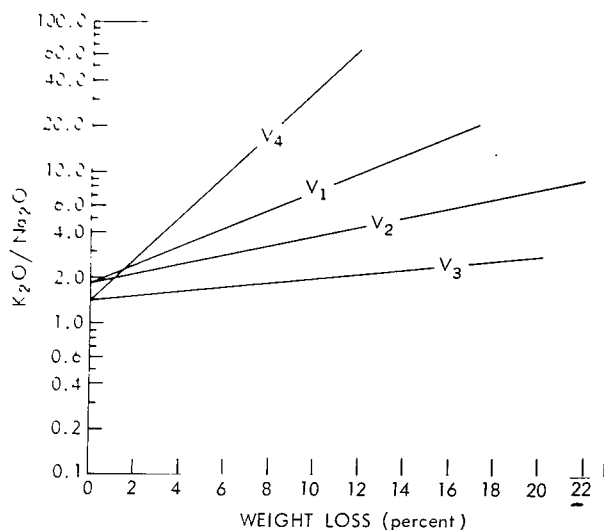


Figure 10—The ratio of K_2O to Na_2O in the run products. The ratio increases constantly with decreasing oxygen fugacity.

Removal of oxygen into a rarified atmosphere is also questionable since the conditions of V_2 included a pressure of approximately 10^{-6} atm, and the material nevertheless was oxidized. Reduction of the parent tektite material by reaction with a metallic meteorite faces the objection of the high chromium to nickel ratio of tektites. Two possibilities are open to explain the ferric-ferrous ratios in the light of the experimental data. Most obvious is that tektites were formed under reducing conditions similar to those of V_1 , perhaps at the lunar surface. An alternative is that the parent material was, indeed, oxidized but initially had a lower ferric-ferrous ratio than that observed in tektites. It may be that the rocks of the moon, having experienced a one-way degassing process, have, at least

near the surface, a deficiency of oxygen. This might even result in the abundance of species such as SiO at the lunar surface. Therefore it may have been that such material was oxidized in the terrestrial atmosphere but did not have enough time to achieve equilibrium.

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